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(54) INTEGRATED SYSTEM FOR THE PRODUCTION OF
CHLORINE DIOXIDE

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INTEGRATED SYSTEM FOR THE PRODUCTION OF CHLORINE DIOXIDE

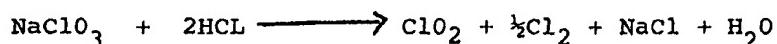
ABSTRACT OF THE DISCLOSURE

A cyclic integrated system for the production of chlorine dioxide utilizes a feed of only chlorine and water. The chlorine dioxide is recovered as an aqueous solution thereof and excess hydrogen is vented from the system. The chlorine dioxide is produced by reduction of sodium chlorate in aqueous acid solution having an acidity of about 0.05 to 1N and using hydrochloric acid as the reducing agent and acid source, the chlorine dioxide being removed in admixture with chlorine and steam evaporated from the reaction medium. The chlorine is separated from the chlorine dioxide and is used to form recycled hydrogen chloride. The sodium chloride formed in the chlorine dioxide-producing reaction is used to form sodium chlorate for recycle.

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The present invention relates to the production of chlorine dioxide, and more particularly to an integrated method of producing chlorine dioxide from hydrochloric acid.

Chlorine dioxide is known to be produced by reduction of an alkali metal chlorate, generally sodium chlorate, using hydrogen chloride as both the reducing agent and source of acidity. The basic reaction involved, in the case where the alkali metal is sodium, is as follows:



10 In the presence of an excess of reducing agent above the stoichiometry of the above equation, a competing reaction occurs:



Since chlorine dioxide is not produced in this latter reaction, in order to maximize chlorine dioxide production, it is preferred to operate at or near the stoichiometry of the first equation in the feed to the reactor.

20 In accordance with the present invention, the production of chlorine dioxide by reduction of sodium chlorate with hydrochloric acid occurs in a cyclic system to which chlorine and water are fed and from which chlorine dioxide, generally as an aqueous solution, and hydrogen are recovered. This is achieved by utilizing the sodium chloride formed in the chlorine dioxide-producing process to regenerate the sodium chlorate consumed, followed by feeding of the sodium chlorate to the chlorine dioxide generator.

The regeneration of the sodium chlorate in the present invention is carried out electrolytically, producing hydrogen as a gaseous product. As indicated above, the



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generation of the chlorine dioxide also produces chlorine which may be separated from the chlorine dioxide. Following recovery of the chlorine, it may be mixed with the added chlorine which chlorine mixture then is reacted with part of the gaseous hydrogen from the electrolytic production of sodium chlorate to form the hydrogen chloride required to react with the regenerated sodium chlorate. The acidity of the aqueous reaction medium is between about 0.05 and 1N, preferably about 0.1 to about 10 0.5N.

The hydrogen chloride may be fed to the chlorine dioxide generator in gaseous form, or may be formed into hydrochloric acid prior to feed to the generator.

The invention is described further by way of illustration with reference to the accompanying drawing, which is a schematic flow sheet of an integrated process in accordance with the present invention.

An integrated chlorine dioxide producing system 10 has infeeds of chlorine by line 12 and water by line 14 20 and produces an aqueous solution of chlorine dioxide in line 16 and gaseous hydrogen in line 18.

Chlorine dioxide is produced in a generator 20 containing an aqueous acid reaction medium having an acidity of from about 0.05 to 1N, by reduction of sodium chlorate, fed as an aqueous solution by line 22, using hydrogen chloride fed by line 24, usually as hydrochloric acid.

The reaction is carried out at an elevated temperature, preferably at the boiling point of the aqueous 30 reaction medium. The water evaporated from the reaction medium by operation at an elevated temperature dilutes

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the chlorine dioxide and chlorine and the resulting gaseous mixture is removed from the generator 20 by line 26.

In order to maintain the reaction medium at a temperature below which substantial decomposition of chlorine dioxide occurs and at the same time maintain the reaction medium at its boiling temperature in order to achieve maximum evaporation of water, the generator is maintained under a reduced pressure.

10 The temperature and pressure conditions may vary widely. Usually the pressure may vary from about 1 to about 700 mm of mercury, preferably from about 50 to about 300 mm of mercury, and the temperature may vary from about 25 to about 100°C, preferably about 40° to about 85°C. As mentioned above, the temperature and pressure parameters are varied interdependently so that the reaction medium preferably is at its boiling point at the absolute pressure in the generator.

20 The level of reaction medium in the generator is maintained substantially constant by balancing the quantity of water removed by evaporation with the quantity of water added with the aqueous sodium chlorate solution and the hydrochloric acid, where gaseous hydrogen chloride is not used.

In addition, where such elevated temperatures and hence evaporation are employed the reaction medium under steady-state conditions usually is saturated with sodium chloride so that product sodium chloride precipitates therefrom.

30 It is possible to operate the generator by removal of an aqueous solution from the reaction medium

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containing spent reactants and sodium chloride. However, it is preferred to operate by precipitation of sodium chloride in the reaction vessel.

The sodium chloride precipitated in the generator 20 is removed, continuously or intermittently, by line 28 and is washed to remove entrained liquor. The spent wash water is returned to the generator. The resulting substantially pure solid sodium chloride is dissolved in water fed by line 14 in a sodium chloride dissolver 30 to form an aqueous solution of sodium chloride of concentration sufficient to be suitable as feed to a chlorate cell. The sodium chloride solution is passed from the dissolver 30 by line 32 to a chlorate cell 34.

10 The chlorate cell 34 may be of any convenient construction to form sodium chlorate electrolytically from the aqueous solution of sodium chloride fed by line 32.

20 The resulting aqueous solution of sodium chlorate is fed by line 22 to the chlorine dioxide generator 10. In practice only part of the sodium chloride content of the aqueous solution fed by line 32 to the chlorate cell 34 is converted to sodium chlorate and hence the sodium chlorate solution in line 22 also contains dissolved sodium chloride. The presence of the sodium chloride in the solution fed by line 22 does not alter the stoichiometry of the system since the chlorate cell 34 under steady-state conditions produces a quantity of chlorate equivalent to that consumed to make chlorine dioxide in the generator and a closed loop of a steady-state amount of excess sodium chloride results.

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The gaseous mixture of chlorine dioxide, chlorine and steam in line 26 is passed to a chlorine dioxide absorber 36 of any convenient construction. Water is fed

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to the absorber 36 which causes condensation of the steam and formation of an aqueous solution of chlorine dioxide which is recovered by line 16 for use in any desired operation. The resultant gaseous chlorine passes from the absorber 36 by line 38.

While a substantial separation of chlorine dioxide and chlorine occurs in the chlorine dioxide absorber 36, generally the chlorine dioxide solution recovered by line 16 contains some dissolved chlorine.

10 The chlorine in line 38 is mixed with chlorine fed by line 12 from any convenient source, such as a caustic soda/chlorine cell and the resulting chlorine stream is fed by line 40 to a hydrogen chloride burner 42.

The electrolytic production of sodium chlorate in the chlorate cell 34 also produces off-gas hydrogen in line 44. About one-third of the mole quantity of hydrogen present in this line is reacted with the chlorine fed to the burner 42 by line 40 to form hydrogen chloride and the remaining two-thirds is discharged from the system by line 18.

20 As illustrated, the hydrogen discharged by line 18 is separated from the hydrogen in line 44 and the remaining one-third mole quantity passes by line 46 to the burner 42. This manner of operation is preferred where the hydrogen chloride produced in the burner 42 is passed directly to the generator 20 by line 24, so that little or no gaseous hydrogen is introduced to the generator 20 with the hydrogen chloride in line 24.

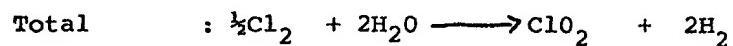
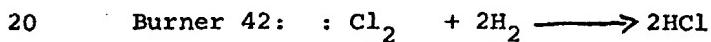
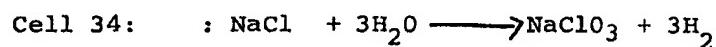
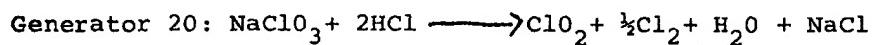
Due to the temperature of the hydrogen chloride discharging from the burner 42 and the cost of cooling the

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gas to a temperature suitable for feed to the generator 20, normally the hydrogen chloride gas is dissolved in water to form hydrochloric acid of the desired concentration which then is passed to the generator 20 by line 24. When the process is carried out in this manner, all the hydrogen in line 44 may be fed to the hydrogen chloride burner 42 so that the hydrogen chloride gas leaving the burner 42 contains the excess hydrogen. Upon formation of the hydrogen chloride gas into hydrochloric acid the excess hydrogen may be vented prior to passage of the hydrochloric acid to the generator 20, so that again hydrogen is not fed to the generator 20.

The excess hydrogen vented from the system by line 18 may be burned with oxygen or in air to form part of the water requirement of the system.

Under steady-state and ideal conditions, the individual reaction involved in the integrated system 10 may be represented by the following equations:



(line 12) (line 14) (line 16) (line 18)

It will be observed that the water fed by line 14 is not the only water utilized in the system 10. However, any additional water fed to the system is balanced by an equivalent amount removed from the system. Thus, the aqueous solution in line 32 must contain more than 3 moles of water per mole of sodium chloride in order to realize an aqueous solution of sodium chlorate in line 22. The excess water

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is evaporated in the generator and leaves the generator as steam. In addition, water introduced to the generator by line 24 where hydrochloric acid is used similarly is evaporated in the generator. Further, spent wash water introduced to the generator 20 after washing of the sodium chloride removed from the generator 20 similarly is evaporated.

As mentioned above, the level of liquid in the generator is maintained substantially constant and thus
10 the steam mixed with the chlorine dioxide and chlorine in line 36 is made up from evaporation of excess water fed with the sodium chlorate solution, excess water fed with the hydrochloric acid, excess water fed as spent wash water and water formed in the chlorine dioxide-producing reaction.

The chlorine dioxide produced in the system
10 is recovered as an aqueous solution thereof in line 16. Water is fed to the chlorine dioxide absorber 36 causing condensation of the steam and dissolving of the chlorine dioxide in water. Hence the chlorine dioxide solution recovered contains all the water contained in the steam and added to the absorber 36. In this way the water introduced to the system 10 excess to the stoichiometric requirements set forth above is removed therefrom as the carrier medium for the chlorine dioxide product.
20

Since the system 10 does not operate at 100% efficient production of ClO_2 or at 100% separation of chlorine dioxide and chlorine, in the operation of the system under practical conditions some adjustment is
30 required.

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The presence of small quantities of dissolved
chlorine in the chlorine dioxide solution in line 16
results

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in a less than stoichiometric quantity of chlorine in line 38. In order to preserve the overall stoichiometry of the system the quantity of chlorine fed by line 12 is increased in proportion to the quantity of dissolved chlorine present in the aqueous chlorine dioxide solution recovered by line 16.

Some of the chlorate in the reaction vessel is converted to chlorine only in accordance with the competing reaction as described above. In order to maintain production 10 of chlorine dioxide at the same level layer quantities of material must be cycled within the system 10 but the overall stoichiometry of the system 10 remain the same, i.e.



Modifications are possible within the scope of the invention.

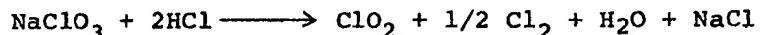
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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An integrated process for the production of chlorine dioxide comprising:

providing an aqueous acid reaction medium having an acidity of about 0.05 to 1N and containing sodium chlorate and hydrochloric acid in the reaction zone,

continuously reducing said sodium chlorate with said hydrochloric acid predominantly in accordance with the equation



thereby continuously generating chlorine dioxide and chlorine, while simultaneously continuously evaporating water from said aqueous reaction medium to form continuously in said reaction zone a gaseous mixture of chlorine dioxide, chlorine and steam,

continuously maintaining said reaction zone under a reduced pressure,

continuously adding sodium chlorate and hydrogen chloride to said reaction medium at rates substantially equivalent to their rates of consumption to form chlorine dioxide and chlorine,

the water being evaporated from said reaction medium at a rate sufficient to maintain a substantially constant volume of aqueous reaction medium in said reaction zone,

removing sodium chloride from said reaction zone either in solid form or in solution in said aqueous reaction medium,

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continuously electrolyzing an aqueous solution of said removed sodium chloride to form an aqueous solution of sodium chlorate and gaseous hydrogen in accordance with the equation



feeding said aqueous solution of sodium chlorate to said reaction medium, the rate of production of sodium chlorate from sodium chloride in said electrolysis being sufficient to maintain said rate of addition of sodium chlorate to said reaction medium,

continuously removing said gaseous mixture of chlorine dioxide, chlorine and steam from said reaction zone, continuously condensing said steam and separating chlorine from said mixture, continuously forming an aqueous solution of said chlorine dioxide containing said condensed steam and removing said aqueous solution of chlorine dioxide,

continuously forming a chlorine reactant stream by mixing feed chlorine with said chlorine separated from the mixture,

continuously reacting the chlorine in said reactant stream with the substantially stoichiometric quantity of hydrogen to form hydrogen chloride in accordance with the equation



the hydrogen reacting with the chlorine being provided by the hydrogen formed in the production of sodium chlorate,

continuously feeding said hydrogen chloride to said reaction medium in gaseous form or as hydrochloric acid, the rate of production of hydrogen chloride, and hence the rate of addition of feed chlorine to the system

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being sufficient to maintain said rate of addition of hydrogen chloride to said reaction medium, and continuously discharging excess hydrogen from the system.

2. The process of claim 1 wherein said reaction medium is saturated with respect to sodium chloride, and including continuously depositing sodium chloride from said reaction medium, removing said deposited sodium chloride from said reaction zone, and continuously forming an aqueous solution of sodium chloride from said removed sodium chloride as said aqueous solution of sodium chloride which is electrolyzed to form sodium chlorate.

3. The process of claim 1 wherein said reaction zone is maintained under a pressure of about 1 to about 700 mm Hg.

4. The process of claim 1, 2 or 3 wherein said reaction medium has a temperature of about 25° to about 100°C.

5. The process of claim 1 wherein said reaction medium is maintained at its boiling point under the absolute pressure of the reaction zone.

6. The process of claim 1, 2 or 5 wherein said reaction zone is maintained under a pressure of about 50 to about 300 mm Hg and the reaction medium is maintained at a temperature of from about 40° to about 85°C.

7. The process of claim 1, 2 or 5 wherein said reaction of chlorine and hydrogen occurs in a combustion zone and all the hydrogen gas formed in said electrolysis

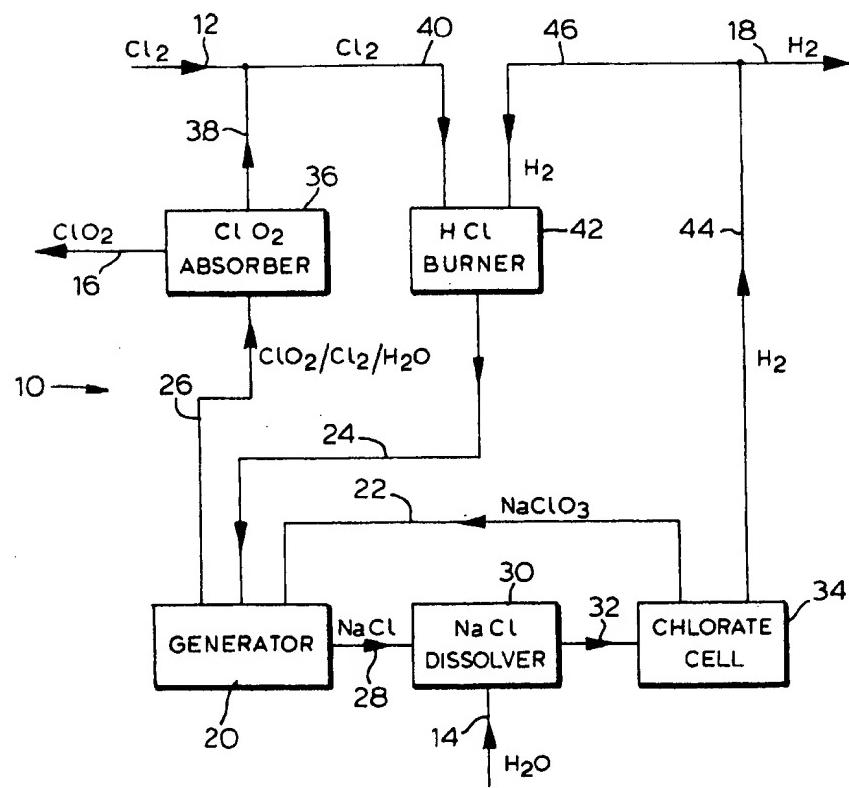
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is passed to said combustion zone whereby there is a considerable excess of hydrogen, and, after formation of said hydrogen chloride, said hydrogen chloride is dissolved in water to form hydrochloric acid and said excess of hydrogen is vented from said hydrochloric acid prior to passage of the hydrochloric acid to said reaction medium as said hydrogen chloride being fed to said reaction medium.

8. The process of claim 1, 2 or 5 wherein said reaction medium has an acidity from about 0.1 to about 0.5 normal.

9. The process of claim 1, 2 or 5 wherein said reaction medium has an acidity from about 0.1 to about 0.5 normal, said reaction zone is maintained under a pressure of about 50 to about 300 mm Hg and the reaction medium is maintained at a temperature of from about 40° to about 85°C.





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